

# Dynamics of the Peierls-active phonon modes in CuGeO<sub>3</sub>

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We reconsider the Cross and Fischer approach to spin-Peierls transitions. We show that a soft phonon occurs only if  $\Omega_0 < 2.2T_{SP}$ . For CuGeO<sub>3</sub> this condition is not fulfilled and the calculated temperature dependence of the Peierls-active phonon modes is in excellent agreement with experiment. A central peak of a width  $\sim 0.2$  meV is predicted at  $T_{SP}$ . Good agreement is found between theory and experiment for the pretransitional Peierls-fluctuations. Finally, we consider the problem of quantum criticality in CuGeO<sub>3</sub>.

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**Introduction** Structural phase transitions come essentially in two varieties, those with a soft phonon mode and those without phonon softening and a central peak [1]. Typically one associates them to displacive and to order-disorder transitions respectively, even though there is no strict formal distinction between displacive and order-disorder transitions. It came then as a surprise that the spin-Peierls transition in CuGeO<sub>3</sub> [2], which had been shown to be displacive [3], shows no phonon softening [3,4]. Even worse, the Peierls-active phonon modes harden by about 5%–6% with decreasing temperature [5]. It has been generally assumed, up to now, that this behaviour is inconsistent with the RPA-approach by Cross and Fischer (CF) to the spin-Peierls transition [6]. Here we show, that the CF-theory is actually fully consistent with the experimental results for CuGeO<sub>3</sub>. We show, that soft phonons occur within RPA only if the bare phonon frequency  $\Omega_0$  satisfies  $\Omega_0 < 2.2T_{SP}$ . For larger phonon frequencies the phonon does not soften and a central peak develops at the spin-Peierls transition temperature,  $T_{SP}$ . We then test the applicability of RPA to CuGeO<sub>3</sub> by calculating the pretransitional Peierls-fluctuations. We find good agreement with experiment. Finally, we note that a key ingredient of the CF-approach, quantum criticality, can be tested for in CuGeO<sub>3</sub>.

**RPA approach** The retarded phonon Green's function  $D_q(\omega)$  is given by [7]

$$D_q(\omega) = \frac{2\Omega_0(q)}{\omega^2 - \Omega_0^2(q) - 2\Omega_0(q)P_q(\omega)}, \quad (1)$$

where  $\Omega_0(q)$  is the frequency of the bare phonon with momentum  $q$ . In RPA one approximates the phonon self-energy  $P_q(\omega)$  by  $g_q^2\chi_q(\omega)$ , where  $\chi_q(\omega)$  is the dynamical energy-energy correlation function and where  $g_q$  is the electron-phonon coupling constant, given by

$$|g_q|^2 = \frac{\lambda^2 \hbar}{M\Omega_0(q)}(1 - \cos(qc)), \quad (2)$$

where we have used

$$\sum_n \lambda(u_{n+1} - u_n)\mathbf{S}_n \cdot \mathbf{S}_{n+1}, \quad (3)$$

for the spin-phonon coupling within a linear-chain model. Here  $\mathbf{S}_n$  are the spin operators at site  $n$ ,  $u_n$  the displacement operators for the normal coordinates of the Peierls-active phonon-mode [5,8] and  $M$  is the effective mass of the normal mode.

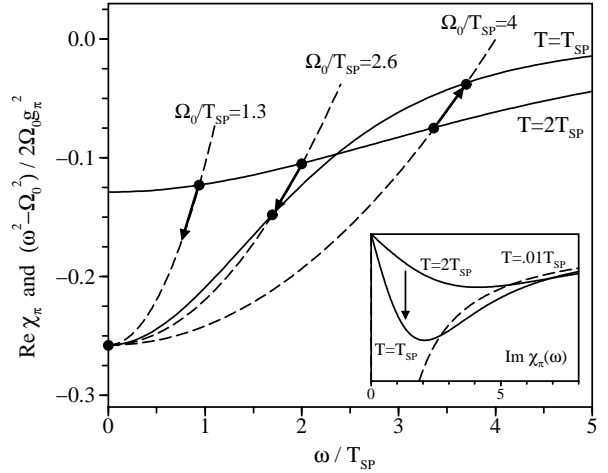


FIG. 1. Plots of  $\text{Re } \chi_\pi(\omega)$  (solid lines) for  $T = T_{SP}$  and  $T = 2T_{SP}$ , as a function of  $\omega/T_{SP}$ . The temperature independent LHS of Eq. (6),  $(\omega^2 - \Omega_0^2)/(2\Omega_0g_\pi^2)$ , is plotted for  $\Omega_0/T_{SP} = 1.3, 2.6, 4$  (dashed lines), with  $g_\pi$  given by Eq. (7). The filled circles denote the position of the phonon frequencies,  $\omega_\pi$ . The arrows indicate the shift of  $\omega_\pi$  with decreasing temperature. Inset:  $\text{Im } \chi_\pi(\omega)$ .

At the spin-Peierls transition a spontaneous dimerization occurs below  $T_{SP}$ , at  $q = \pi/c$ . In the following we set the lattice constant  $c$  to unity in the theory formulas. Cross and Fischer observed, that the correct functional form for  $\chi_q(\omega)$  (in the limit  $\omega \rightarrow 0$ ) can be obtained from bosonization [6],

$$T\chi_q(\omega) = -2d I_1\left(\frac{\omega - \Delta}{2\pi T}\right) I_1\left(\frac{\omega + \Delta}{2\pi T}\right) \quad (4)$$

where  $d \approx 0.37$  is a constant depending weakly on the momentum cut-off,  $\Delta = v_s|q - \pi|$  is the lower edge of the

two-spinon continuum ( $v_s$  is the renormalized spin-wave velocity), and

$$I_1(k) = \frac{1}{2\pi} \int_0^\infty e^{ikx} (\sinh(x))^{-1/2}.$$

$T\chi_{q=\pi}(\omega)$  is scale-invariant and a function of  $\omega/(2\pi T)$  only (independent of the spin-spin coupling  $J$ ). This behaviour is characteristic of quantum critical systems [9]. For any temperature  $T > 0$  we can expand  $T\chi_\pi(\omega)$  in  $\omega/(2\pi T)$  as

$$T\chi_\pi(\omega) = -\chi_0 - i\chi_1 \left(\frac{\omega}{2\pi T}\right) + \chi_2 \left(\frac{\omega}{2\pi T}\right)^2 + \dots, \quad (5)$$

with  $\chi_0 \approx 0.26$ ,  $\chi_1 \approx 0.81$  and  $\chi_2 \approx 2.2$ . The position of the poles  $\omega_\pi$  of  $D_\pi(\omega)$  are then determined by the roots of

$$\frac{\omega^2 - \Omega_0^2}{2\Omega_0 g_\pi^2} = \text{Re}\chi_\pi(\omega) \approx -\frac{\chi_0}{T} + \frac{\chi_2}{T} \left(\frac{\omega}{2\pi T}\right)^2, \quad (6)$$

where  $\Omega_0 \equiv \Omega_0(\pi)$ . Typical plots of the left and right hand side of (6) are presented in Fig. 1.

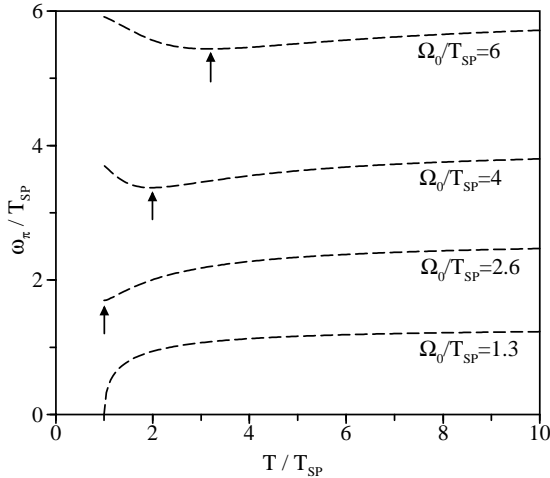


FIG. 2. The temperature dependence of the phonon frequencies  $\omega_\pi$  for various values of  $\Omega_0/T_{SP}$ .  $\Omega_0$  is the bare phonon frequency. The arrows indicate the respective minimal phonon frequency.

A spontaneous lattice dimerisation, i.e. a macroscopic occupation of the Peierls-active phonon mode, occurs at  $T_{SP}$  when (6) has a solution for  $\omega = 0$ . This determines the transition temperature as [6]

$$T_{SP} = \frac{2g_\pi^2}{\Omega_0} \chi_0. \quad (7)$$

Remarkably, Eq. (7) is independent of  $J$ , due to the scale-invariance of  $T\chi_\pi(\omega)$ . We compare the prefactor of the terms  $\sim \omega^2$  of the rhs and lhs of Eq. (6) and find that for

$$1/(2g_\pi^2\Omega_0) > \chi_2/(4\pi^2 T_{SP}^3), \quad (8)$$

Eq. (6) has a single solution for  $T = T_{SP}$  and inspection of the temperature dependence of this solution for  $T > T_{SP}$  (compare Fig. (1)) shows that this root continuously connects to the  $T = \infty$  solution,  $\lim_{T \rightarrow \infty} \omega_\pi = \Omega_0(\pi)$ . In the parameter regime defined by Eq. (8) the phonon softens completely. We can use Eq. (7) to eliminate  $g_\pi$  from Eq. (8). We obtain

$$T_{SP} > \frac{\Omega_0}{2\pi} \sqrt{\frac{\chi_2}{\chi_0}} \approx 0.46 \Omega_0, \quad \Omega_0 < 2.2 T_{SP}, \quad (9)$$

for the soft-phonon regime. For  $\Omega_0 > 2.2 T_{SP}$  the Peierls-active phonon does not soften completely and may even become harder with decreasing temperature, as illustrated in Fig. 2. Near  $T = T_{SP}$  an additional central peak shows up, leading to the phase transition. For CuGeO<sub>3</sub> there are two Peierls-active phonon modes with energies [5]  $\omega_1 = 151$  K and  $\omega_2 = 317$  K respectively. Since (see below)  $\Omega_\gamma \approx \omega_\gamma$  ( $\gamma = 1, 2$ ) and  $T_{SP} = 14.1$  K we find that CuGeO<sub>3</sub> is in the central-peak regime.

*Application to CuGeO<sub>3</sub>* In order to compare more in detail with the experimental results for CuGeO<sub>3</sub> we have generalized Eq. (1) for the case of two phonon frequencies. Denoting by  $D_{1/2}(\omega)$  the retarded Green's functions of the first and second phonon with bare frequencies  $\Omega_1$  and  $\Omega_2$  respectively, and by  $g_1$  and  $g_2$  the respective spin-phonon coupling constants, we obtain

$$D_1(\omega) = D_1^{(0)}(\omega) + \frac{\left(D_1^{(0)}(\omega)\right)^2 g_1^2 \chi_\pi(\omega)}{1 - \left(g_1^2 D_1^{(0)}(\omega) + g_2^2 D_2^{(0)}(\omega)\right) \chi_\pi(\omega)}$$

and an equivalent equation for  $D_2(\omega)$ . Here  $D_{1/2}^{(0)}(\omega) = 2\Omega_{1/2}/(\omega^2 - \Omega_{1/2}^2)$  [7]. An analysis similar to the one-phonon case can be performed for  $D_1(\omega) + D_2(\omega)$ . One finds

$$T_{SP} = \left(\frac{2g_1^2}{\Omega_1} + \frac{2g_2^2}{\Omega_2}\right) \chi_0 \quad (10)$$

for the transition temperature and

$$T_{SP} > \sqrt{\frac{\chi_2}{\chi_0}} \frac{\Omega_1 \Omega_2}{2\pi} \sqrt{\frac{g_1^2 \Omega_2 + g_2^2 \Omega_1}{g_1^2 \Omega_2^3 + g_2^2 \Omega_1^3}} \quad (11)$$

for the soft-phonon regime.

In order to determine  $g_1$  and  $g_2$  for CuGeO<sub>3</sub> we note that the lower/upper phonon mode contribute to the structural distortion below  $T_{SP}$  with weighting factors 2 and 3 respectively [5]. This leads to

$$\frac{g_1^2/\Omega_1}{g_2^2/\Omega_2} = \frac{2}{3}, \quad \frac{g_1^2}{g_2^2} = \frac{2\Omega_1}{3\Omega_2} \approx \frac{2\omega_1}{3\omega_2} \approx \frac{1}{3}. \quad (12)$$

Eq. (12) and Eq. (10) determine the spin-phonon couplings  $g_1$ ,  $g_2$ . For  $T_{SP} = 14.1$  K we find  $\Omega_1 = 3.15$  THz

and  $\Omega_2 = 6.61$  THz for the bare phonon frequencies and  $g_1 = 0.86$  THz ( $g_2 = \sqrt{3}g_1$ ) for the spin-phonon coupling.

In Fig. 3 we have plotted the results for the dynamical structure factor,

$$S(\pi, \omega) = -\frac{1}{\pi} \frac{\text{Im}[D_1(\omega + i\delta) + D_2(\omega + i\delta)]}{1 - \exp(-\beta\omega)}, \quad (13)$$

where we have used the experimental resolution function [THz]  $\delta \approx 0.023 + 0.028\omega/(2\pi)$  [10]. The intensity of the experimental spectra [5], also shown in Fig. 3, have been scaled; the (constant) background has been adjusted [11]. The overall agreement between experiment and theory is satisfactory, although the hardening of the lower phonon mode is somewhat more pronounced in the experiment (6% vs. 1%). No experimental data for the upper mode were available for  $T = 16$  K. In the inset a blowup of the central peak is given. It should be possible to resolve the predicted central peak, which has a width of  $\approx 0.05$  THz = 0.2 meV, by neutron scattering, testing thereby the theory.

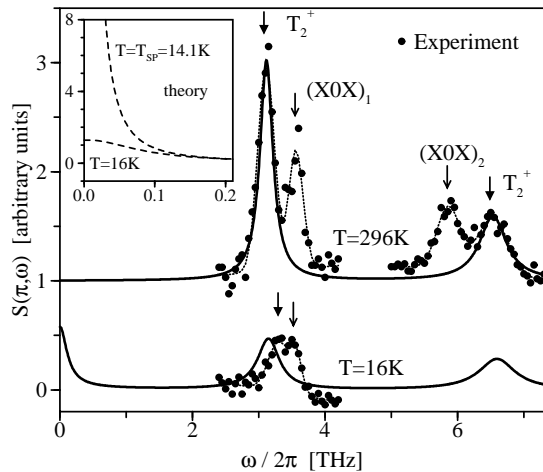


FIG. 3. Theoretical (thick solid lines) and experimental (solid circles, [5]) results for the dynamical structure factor. The  $T_2^+$  phonons are Peierls active and included in the theory,  $(XOX)_1$  and  $(XOX)_2$  are other nearby phonons. The data for  $T = 296$  K has been shifted. Inset: Blowup of the central peak at  $T = T_{SP} = 14.1$  K and  $T = 16$  K (not broadened).

The theory presented here is based on the RPA approximation and we have shown it to yield reasonably good agreement with experiment, explaining the absence of a Peierls-active soft-phonon mode in CuGeO<sub>3</sub>. From a theoretical point of view, one might question the applicability of RPA in the central-peak regime. A definite theoretical resolution to this problem is not known at present, but one may note that the standard phenomenological theory for the central peak occurring in structural phase transitions has RPA-form [1]. For the case of CuGeO<sub>3</sub> we will test the applicability of RPA by comparing the

prediction of RPA (with no fit parameter) for the pretransitional Peierls-fluctuations, given by the inverse lattice correlation length  $1/\xi$ , with the experimental results.

The lattice correlation length is determined by the long-distance falloff,

$$\lim_{z \rightarrow \infty} \int \frac{dq}{2\pi} e^{iqz} \text{Re} D_q(0) \sim e^{i\pi z/c} e^{-z/\xi}, \quad (14)$$

where  $c = 2.94$  Å is the  $c$ -axis lattice constant of CuGeO<sub>3</sub> and  $D_q(\omega) = \sum_{\gamma} D_{q,\gamma}(\omega)$ . We have calculated  $1/\xi$  from Eq. (14), using  $v_s = (\pi/2)J(1 - 1.12\alpha)$  [12] (which enters Eq. (4)),  $J = 156$  K for the exchange integral and  $\alpha = 0.24$  for the frustration parameter [13–15]. The results for  $1/\xi$  are presented in Fig. 4, together with results for CuGeO<sub>3</sub> obtained by diffusive X-ray scattering [16], which are consistent with neutron-scattering data and the absence of a soft phonon [3].

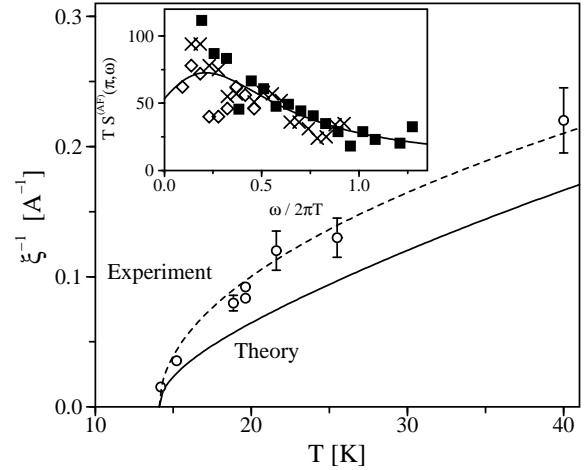


FIG. 4. RPA and experimental results [16] for the inverse lattice correlation length,  $1/\xi$ . The theory does not contain any free parameter. Inset:  $TS^{(AF)}(\pi, \omega)$ , as a function of  $\omega/(2\pi T)$ , as predicted by bosonization (solid line, Eq. (4)), and the neutron-scattering results [3], for  $T = 14.5$  K (filled squares),  $T = 20$  K (crosses) and  $T = 50$  K (diamonds).

Both experiment and theory show mean-field behaviour,  $1/\xi \sim \sqrt{T - T_{SP}}$ . The RPA-result agrees well with experiments. Above  $T = 19$  K the lattice fluctuations have one-dimensional character [16] and the residual difference between theory and experiment may be due to corrections to RPA.

It is interesting to note, that Eq. (4) for  $\chi_q(\omega)$  is (for spin-rotational invariant Heisenberg chains) identical with the bosonization result for the magnetic dynamical structure factor,  $S^{(AF)}(q, \omega)$  [17]. Quantum criticality implies  $TS^{(AF)}(\pi, \omega)$  to be an universal function of  $\omega/(2\pi T)$ , at least for small  $\omega$ . In the inset of Fig. 4 we have plotted the bosonization result for  $TS^{(AF)}(\pi, \omega)$ , together with the rescaled neutron-scattering results [3]

We observe that the experimental data approximately obey the scaling, though there is substantial scattering of the data for small  $\omega/(2\pi T)$ , possibly influenced by non-critical contributions from the Peierls-fluctuations or by a crossover of the character of the magnetic excitations from 1D to 2D near the Peierls transition [14]. It is also interesting to note, that the prediction for  $T S^{(AF)}(\pi, \omega)$  is independent of  $J$  and that the data for other 1D Heisenberg antiferromagnets with very different values of the coupling  $J$ , like  $\text{KCuF}_3$  [18], should fall onto the same universal curve presented in the inset of Fig. 4. An experimental verification of quantum criticality for  $S^{(AF)}(\pi, \omega)$  would imply also scale-invariance for  $\chi_\pi(\omega)$ , since both coincide within bosonization [6,17].

*Generalization* Until now we assumed spin-rotational invariance. Next we will show, that a central-peak regime occurs also in spin-Peierls transitions lacking spin-rotational invariance. An example is the spin-Peierls transition in a system of phonons coupled to an array of chains with Ising spins. This model was solved exactly by Pytte [19]. It contains a parameter regime, where the transition is displacive and phonons do not become soft. In the opposite limit, when the spin-chains are xy-like, the transition corresponds via the Jordan-Wigner transformation to the standard Peierls transition [20]. Again one can show [21], that soft-phonons occur in RPA, e.g. for  $T_{SP} = J/10$ , only for  $\Omega_0 < 0.8J$ . For  $\Omega_0 > 0.8J$  the Peierls-active phonon does not become soft and a central peak arises at  $T_{SP}$ .

*Discussion* In this letter we have shown, that the RPA approach to the spin-Peierls transition includes both a soft-phonon and a central-peak regime. This result is at first sight counterintuitive, as continuous lattice distortions below  $T_{SP}$  are generally associated with a softening of the lattice above  $T_{SP}$ .

The eigenstates of the spin-phonon system evolve adiabatically as a function of the spin-phonon coupling strength in the soft-phonon regime. In the central-peak regime a new magnetophonon appears at low frequencies and condenses at  $T_{SP}$ , leading to the structural transition and the formation of spin-singlets. This new collective excitation is a superposition of a phonon with two magnons in a singlet state. The magnetophonon couples to the phonon propagator and therefore shows up as a low-energy resonance in  $D_q(\omega)$ , the central peak. The other resonance in  $D_q(\omega)$ , at  $\omega_\pi$ , has the limit  $\lim_{g_\pi \rightarrow 0} \omega_\pi = \Omega_0(\pi)$ . Therefore, one usually regards  $\omega_\pi$  to be the “true” phonon frequency. In terms of the eigenstates of the coupled spin-phonon system such a distinction does not make sense. In the central-peak regime the spectral weight of  $D_q(\omega)$  is divided in between the “phonon-resonance” at  $\omega_\pi$  and the soft magnetophonon.

*Conclusions* The absence of a soft Peierls-active phonon mode in  $\text{CuGeO}_3$  has been considered as a challenge to theory. It has been argued [22] that the Cross and Fischer theory is essentially incomplete, i.e. not ap-

plicable to  $\text{CuGeO}_3$ . Here we point out, that the absence of soft phonons does actually find a natural explanation within the CF-approach. The calculated temperature-dependence of the phonon modes and that of the pre-translational Peierls-fluctuations are in excellent agreement with experiment. A central peak of width 0.2 meV is predicted to appear at  $T_{SP}$ . Finally we have pointed out, that a key ingredient of the theory, the quantum criticality of  $\chi_\pi(\omega)$ , can be tested, albeit indirectly, with neutron scattering through a test of the scale invariance of the magnetic dynamical structure factor,  $S^{(AF)}(\pi, \omega)$ .

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